

# Atomic Chain Electronics

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Adatom chains, precise structures artificially created on an atomically regulated surface, are smallest possible candidates for future nanoelectronics. Since all the devices are created by combining adatom chains precisely prepared with atomic precision, device characteristics are predictable, and free from deviations due to accidental structural defects. In this atomic dimension, however, an analogy to the current semiconductor devices may not work. For example, Si structures are not always semiconducting. Adatom states do not always localize at the substrate surface when adatoms form chemical bonds to the substrate atoms. Transport properties are often determined for the entire system of the chain and electrodes, and not for chains only. These fundamental issues are discussed, which will be useful for future device considerations.

## I. Introduction

When the transistor size is reduced below  $0.1\ \mu\text{m}$ , there arise a lot of unwanted effects which will lead to malfunctioning of devices. It has been pointed out<sup>1</sup> that the spatial fluctuation of dopant atoms would be a serious problem in the sub- $0.07\ \mu\text{m}$  gate length regime. The number of dopant atoms in the channel in such a small device is typically less than a hundred and electrons see discrete dopant atoms that are scattered randomly inside the channel. This causes significant deviation in input/output characteristics from device to device even though the devices are designed and fabricated in the same way, thus placing limitation for integration. Controlling dopant positions is possible to some extent, but atomic scale control is practically impossible.

One fundamental solution to this problem is to create electronics that are atomically precise, ordered, but preferably simple. Atomic chains are precise structures with adatoms created on an atomically regulated surface using atom manipulation technology,<sup>2</sup> and are candidates for constituent components in future nanoelectronics. All adatoms will be placed at designated positions on a substrate, and all device structures are precise, hence free from any accidental, statistical defects. This scheme aims at smallest possible electronics, but we do not know to what extent the common sense of current semiconductor devices survive. This includes fundamental issues of what are metallic and semiconducting structures, what kind of substrate is appropriate for mounting atoms, or the relation between the band picture and the Coulomb blockade picture.<sup>3</sup> Before considering how to miniaturize devices to atomic dimensions, it is necessary to clarify them, where analogies to the current devices may not work.

In this article, we will mainly focus on the electronic properties of adatom structures and discuss how they are different from their macroscopic counterparts. It is shown that a one-dimensional

array of Si atoms is not semiconducting, but metallic, regardless of the lattice spacing, if Si atoms do not form any chemical bonding to the substrate atoms and are isolated.<sup>4</sup> Even two-dimensional square arrays or three-dimensional cubic arrays (if such crystals existed) are not semiconducting. Only a usual diamond-structure Si crystal is semiconducting due to the  $sp^3$ -hybridization that can accommodate all the electrons without leaving any part of the orbitals. The situation differs if we allow chemical bonding to the substrate atoms. A Si chain is semiconducting when there are two chemical bonds per Si atom to the substrate atoms. Similarly, a chain with group III adatoms with a chemical bond each, or the one with group II adatoms with no chemical bond is semiconducting.<sup>5</sup>

From an application point of view, this chemical bonding scheme provides good stability of adatom structures. The typical chemical bond energy is several eV so that adatoms do not move around on the surface even at room temperature. However, there is a concern about electronic isolation.<sup>5</sup> The wave functions may not be restricted on the adatom structures, but penetrate deep into the substrate through chemical bonds, leading to unwanted crosstalk between independent chains. Depending on the nature of the substrate, this is or is not the case.

In this atomic dimension, the contact between the chain and electrodes sometimes play a decisive role.<sup>6</sup> When the electron exchange across the contact is rare, electrons tunnel from an electrode to the chain, and from the chain to the other electrode one by one in a space-correlated manner. The  $I$ - $V$  characteristics will show a Coulomb staircase shape, and the step voltage is determined by two contact capacitances only. In this case, the contact capacitances rather than the chain itself determine the  $I$ - $V$  characteristics. Only when the electron exchange is frequent, the predicted band structure has a realistic meaning.

In Sec. II, Si structures are studied in detail focusing on when they become semiconducting. In Sec. III, substrate effects are briefly discussed and in IV. contact is considered. Summary is given in Sec. V.

## II. Metallic and Semiconducting Si Structures

In atomic scale structures, the macroscopic electronic properties are not necessarily reflected. For example, we may tend to think Si structures with atomic scale will also be semiconducting, but this is not correct. One-dimensional Si chains, if we can force such a geometry by applying an external force, are metallic regardless of the lattice spacing.<sup>4</sup> This is shown using a tight-binding method with universal parameters.<sup>7</sup>

This result can be interpreted with a following picture. In a chain atom, an s-orbital and three p-orbitals are hybridized to have two s-p orbitals along the chain and two p-orbitals perpendicular to the chain. Two facing s-p orbitals of two neighboring atoms (one from each) form bonding and antibonding orbitals. As a result, there are one bonding orbit ( $1/2 \times 2$ ), one antibonding orbit ( $1/2 \times 2$ ), and two p-orbitals per atom. After the formation of a chain structure, each orbital has a finite width: the bonding orbital becomes a valence band, the antibonding orbital becomes a conduction band, and the two p-orbitals become two degenerate  $\pi$ -bands. Two electrons occupy the valence band completely, and the remaining two occupy a part of the conduction band and the  $\pi$ -bands, so

that the Fermi energy is located somewhere in the conduction band. Therefore, the chain is metallic. Since the filling is not exactly  $1/2$  or  $1/3$ , Mott or Peierls transitions<sup>8</sup> are not relevant. The lattice spacing simply modulates the band widths, so that the result is independent of it.

The dimensionality is not the essence. Two-dimensional Si arrays, if atoms are forced to have this geometry, are again metallic.<sup>4</sup> We may want to think that there are four nearest neighbors and they accommodate four valence electrons, resulting in a semiconductor, but this is not what happens. Regardless of the lattice spacing, the  $\pi$ -band originating from the p-orbitals perpendicular to the plane always appear inside the conduction band, and the Fermi energy is located inside the  $\pi$ -band. The same can be expressed such that low energy orbitals are not parallel to  $x$ - and  $y$ -axes. Even if we were able to create a three-dimensional cubic crystal with Si atoms, it would still be metallic regardless of the lattice spacing, since there are six nearest-neighbor atoms for only four valence electrons.

The reason a diamond-structure Si crystal is semiconducting is because four valence electrons are appropriately accommodated in four  $sp^3$ -orbitals forming four covalent bonds per atom (in fact, eight electrons for eight  $sp^3$ -orbitals per unit cell). The same thing can be viewed differently in a gedanken experiment of changing the lattice spacing from infinity to a finite value and forming a crystal from independent atoms.<sup>9</sup> When the lattice spacing is huge, we have 3s and 3p discrete energy levels (one 3s and three 3p states). The band gap corresponds to the 3s and 3p level separation. As the spacing is reduced, each level has a finite width and forms a band, separated by an only band gap. When the spacing is further reduced, one of the upper bands (p-origin) and the lower band (s-origin) touch. This is an s-p crossing and an onset of  $sp^3$ -hybridization. After this crossing, a new band gap appears changing the partition of these bands. Now, there are two lower bands and two upper bands, separated by the new band gap. The former two bands become the valence bands accommodating four electrons and thus completely full, and the latter two bands become the conduction bands accommodating no electrons and thus empty. The usual diamond-structure Si crystal is semiconducting since the natural lattice spacing corresponds to this region.

In short, the  $sp^3$ -hybridization is the key for the semiconducting behavior of Si. We may not expect this in artificial chain structures if there is no chemical bonding between the chain atoms and substrate atoms. However, the situation is different if there is. For example, if a Si atom forms two chemical bonds to the substrate atoms, then the adatom chain may be semiconducting.<sup>5</sup> On a (100) unreconstructed surface of a diamond-structure crystal, a Si adatom has a final configuration of  $sp^3$   $sp^3$ ,  $sp$ , and  $p$  orbitals. Two  $sp^3$ -orbitals are used for chemical bonds (covalent bonds) with the substrate atoms, and the  $sp$ - and  $p$ -orbitals form (adatom, not bulk) valence and conduction bands, respectively. The covalent bonds have a much lower energy than the conduction and valence bands, and therefore these two electrons cannot contribute to the chain properties. The remaining two electrons can determine the adatom chain properties, and fill the valence band completely, while leaving the conduction band empty. Similarly, we can expect a semiconducting chain with group III adatoms with one chemical bond to a substrate atom, or with group II adatoms with no chemical bond.<sup>5</sup>

### III. Substrate Effects - Adatom Surface States

An ideal substrate for atomic chain electronics must serve as a non-interacting template: it holds adatoms with a reasonable potential barrier to suppress unwanted displacement and achieve structural stability, and keeps chains electronically isolated from the substrate and from other chains. These two requirements conflict. For isolation, we may forbid chemical bonding, so that adatom systems are isolated from the substrate, but then the only physical mechanism to hold adatoms is a van der Waals force. The force is estimated to be generally weaker than a thermal energy at room temperature and this scheme will not be suitable.<sup>5</sup> For stability, we can allow chemical bonding to the substrate atoms so that adatom positions are secured. Since a typical chemical bond has an energy of several eV, adatoms will not wander on the surface even at room temperature. In turn, a main concern is electronic isolation. The surface localized modes are not always supported and independency of different chains may not be guaranteed. In the worst scenario, independent adatom structures interact strongly through an overlap of wave functions deep inside the substrate, leading to poor electronic isolation.

This problem is studied with one-dimensional models, and conditions for edge states to localize mostly at edge atoms are clarified.<sup>5</sup> Figure 1 shows the molecular energy levels of an atomic chain with the finite number of atoms as a function of lattice spacing. (a) is a plot for 24 atom Si chain, where an s-orbital and a p-orbital are taken into account. The remaining p-orbitals are assumed to be used for covalent bonding in a realistic crystal. As the lattice spacing is reduced from infinity, the energy levels spread, but there are no states within the band gap. As the spacing is reduced, at around 2.7 Å, there is an s-p band crossing. For further reduction, there appear Shockley surface states in the band gap. (b) shows the electron existence probability at the edge atoms for these modes shown with thick lines in (a). It is noted that the electrons localize strongly at the edge atoms. We can make a general statement depending on the natural lattice spacing is either before or after than the s-p crossing point. If the substrate is composed of materials with s-p crossing bands,<sup>7</sup> such as Si, Ge, or GaAs with diamond or zinc-blend structures, then dangling-bond states at edge atoms localize strongly.<sup>5,9</sup> These states are sandwiched by the vacuum barrier and the bulk band gap, and decay exponentially into the substrate. If the substrate is an alkali halide crystal with uncrossing bands such as LiF or KCl, all the states penetrate deep into the bulk and there are no edge states. This sharp contrast is because the edge states are significant mixture of s- and p-orbitals. When the lattice spacing is large, there is no way for s- and p-orbitals to mix effectively form edge states.

Edge states can be manipulated with H atoms. Figure 1 (c) and (d) are the same set of plots for a chain with 22 Si atoms with edge atoms saturated with H atoms. On an s-p crossing substrate, unsaturated dangling bonds create edge states, but saturation with H atoms eliminate them. This relation reverses on an s-p uncrossing substrate: we have edge states for dangling bonds saturated with H atoms, but do not have any for those unsaturated. This complimentary behavior of H-saturated cases is related to whether the wave function can connect smoothly into the vacuum or not, and is consistently understood<sup>5</sup> in a gedanken experiment of reducing the lattice spacing from infinity to a finite value as the crystal is formed from an independent separated atoms. In fact, the role of the H atom is to flip the derivative of the Bloch wave function without changing the value in the last unit cell facing the vacuum. This is possible since the H atom provides only one atomic state with even parity, 1s, as far as electronic properties are concerned.

The numbers in the plots indicate the number of states. Assuming two electrons are provided for the chain bonding, and two are used for chemical bonding with neighboring atoms in a realistic three-dimensional substrate crystal, 24 states are filled for the 24 Si chain and therefore the edge states are half filled. Similarly the edge states for the H-saturated chain is also half filled since 23 states must be filled, counting an electron from each H atom. The Peierls transition is not relevant in practical situations, since unused dangling bonds on the substrate surface may be saturated with H atoms. These H atoms will absorb electrons, reflecting the atomic level difference compared to the those of substrate atoms, and the filling is a little off from the exact one half. When adatoms are different kinds of atoms than the substrate atoms, this trend will be more evident.

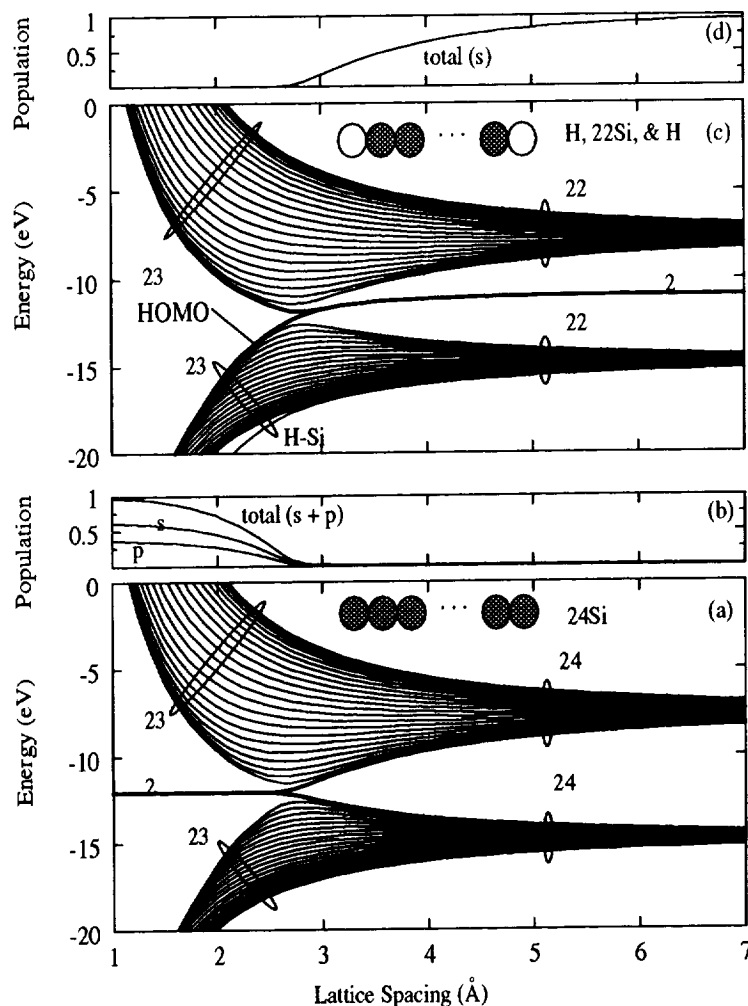


FIG. 1. Molecular energy levels and electron population: (a) energy levels and (b) population for 24 Si chain; (c) energy levels and (d) population for 22 Si chain with H-saturation.

The same conclusions for the existence of edge states on s-p crossing and uncrossing substrates apply for dangling bond states created on an adatom chemically bonded to substrate atoms, if adatoms and substrate atoms have close atomic energy levels. If not, there would be edge states orig-

inated from the atomic states on an uncrossing crystal. Another complication is that even though there exist edge states for a single adatom, after formation of adatom chains, the adatom band structure may be well beyond the bulk band gap. This does not immediately mean that adatom modes are mixed with the bulk modes, but may be a potential problem in the future, and need further study.

#### IV. Band and Coulomb Blockade Pictures

Transport properties in principle reflect the band structure of a chain but not in the same way as in the macroscopic cases. In this atomic dimension, the contact between the chain and electrodes often plays an decisive role. There are two limits for the contact.<sup>6</sup>

If the contact allows frequent electron exchange (no potential barrier for electrons), then the wave function can spread coherently over the entire system. In this case, the expected number of electrons on the chain system will take a continuous value since they co-exist over the chain and electrodes. This makes the discrete nature of electrons irrelevant, and the transport can be described by a continuous-fluid picture, possibly with a correlated-electron model.<sup>10</sup> The finiteness of the number of chain atoms will not play a crucial role since the chain edges are virtually extended smoothly in the electrodes. Therefore, the band picture prevails and the Coulomb blockade<sup>3</sup> is not important. The spin degeneracy is preserved and one state can accommodate two electrons with spin up and down.

In the other limit of infrequent electron exchange (high barrier for electrons), the chain system is isolated from the electrodes. The expected number of electrons on the chain has to be quantized, taking only integer values, and electrons will cross the contact one by one. The expected  $I$ - $V$  characteristics of a chain with two electrodes, or equivalently two small capacitances in series, are known to show a Coulomb staircase, due to the spatially correlated electron tunneling of electrons through capacitances. The effective energy levels at the chain part are discrete, and the level spacings are determined by size quantization and Coulomb interaction. The spin degeneracy is lifted, so that one energy level can accommodate only one electron.

If we choose to use various concepts in current semiconductor devices, we need to establish a method to obtain contact with frequent electron flow, otherwise the entire electronics must be created with Coulomb blockade devices. Obtaining good contact is not trivial since there would generally be a potential barrier at junctions where two different chains meet. With good contact, conductance for a metallic chain is expected to be quantized in the multiples of  $2e^2/h$  under low bias conditions as in mesoscopia, although the correlated-electron effects<sup>10</sup> may modify it to some extent. This is at least not contradictory to the experimental findings of conductance values around  $2e^2/h$ , where metallic wires with atomic scale widths were realized when macroscopic wires were stretched quite close to disconnection.<sup>11</sup> In these atomic wires, the chain part and the electrode parts were realized monolithically, and the contact was gradually tapered so that the system could be regarded as a metallic chain with good contact. In this sense, these experiments are related to, but do not precisely correspond to our situation. In fact, the geometry of these experiments are not quite one-dimensional as discussed here, and we cannot completely exclude such

probability that they have observed, e.g., bimodal transmission in the diffusive regime, and the correlated electron effects are not differentiated, either.

## V. Summary

Nanoelectronics with precise adatom structures are discussed. This is the smallest possible electronics, but the various common sense from current semiconductor devices has to be re-examined. Unlike the macroscopic counter part, Si structures are mostly metallic since  $sp^3$ -hybridization is not achieved. Si chains can be semiconducting only if a Si atom form two chemical bonds with the substrate atoms, where  $sp^3$ -hybridization are forced (and for dangling bonds, rehybridization results to have  $sp$ - and  $p$ -orbitals). We may tend to think that all the dangling bonds of an adatom unconditionally localize at the surface, but this is true only on an  $s$ - $p$  crossing substrate surface such as Si, Ge, or GaAs. On an uncrossing substrate surface such as LiF or KCl, the dangling bond states penetrate deep into the bulk substrate and do not localize. Transport properties are determined only for the combined system of the chain and electrodes. Their contact is extremely influential for the  $I$ - $V$  characteristics. For good contact, the band picture prevails and the finite length of the chain does not play an important role. For poor contact, the  $I$ - $V$  characteristics are determined not by the adatom band properties but two capacitances at the electrode contacts. These fundamental understandings are important in considering how to miniaturize devices to atomic dimensions.

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